Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. II. Cracking Mechanism on the Pt-silica Gel Catalyst.

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In the previous paper the optimum analytical conditions were searched and found to lie within the definite ranges out of which the experimental values obtained were always lower than the calculated ones. We are going to explain the reasons for these by the experimental results and theoretical considerations.

I. Heating Rate of the Sample. When the rates of heating the sample are different the mean partial pressures of carbon oxides produced in the cracking zone will be also different; and slower the heating rate, more favourable it is for the complete reduction of carbon oxides. The temperature of the small outlet tube, on the inside wall of which the reduction water is condensed, is estimated to be around 40°–50°C. and, therefore, the mean partial pressure of water vapour produced and then the mean ratios of hydrogen to carbon monoxide and carbon dioxide are estimated to be around 14 and 25 respectively.

II. Cracking on the Pt-silica Gel Catalyst. (1) *Experimental Procedure.* The vapours produced from the sampling boat are normally heated to 950°C. on the Pt-silica gel catalyst and are completely decomposed to carbon monoxide, carbon dioxide and water vapour. The nickel catalyst which reduces the carbon oxides thus produced is removed from the reaction tube, intending to see the reaction course in the cracking zone. The water produced is caught by calcium chloride and the carbon dioxide by 50% potassium hydroxide solution.

(2) *Influence of Cracking Temperature.* The results on saccharose are given in Table 4.

Table 4. The influence of cracking temperature on the distribution of oxygen in the various products.

Sample saccharose (Oxygen % = 51.43), heating temp. of sample saccharose 950°C., hydrogen velocity 4 l./hr., analytical period, 60 min..

Expt. No.	Temp. of Pt-silica gel °C.	Sample g.	H_2O produced %	CO_2 produced %	Oxygen balance, %			
					to H_2O	to CO_2	to CO	Undecomposed
C-18	800	0.1526	30.34	5.77	52.38	8.17	37.04	2.41
C-32	850	0.1777	28.19	5.46	48.69	7.72	41.63	1.96
C-15	860	0.1668	27.04	4.98	46.68	7.04	44.32	1.96
C-16	860	0.1486	27.05	5.18	46.70	7.33	44.01	1.96

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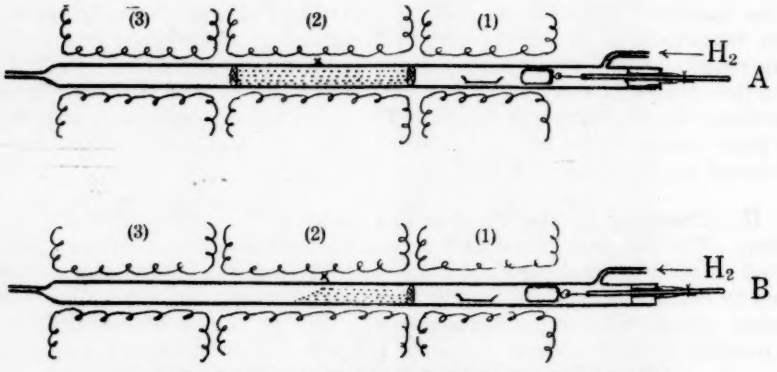
Table 4.—(*Concluded*)

Expt. No.	Temp. of Pt-silica gel °C.	Sample g.	H_2O produced %	CO_2 produced %	Oxygen balance, %			
					to H_2O	to CO_2	to CO	Undecomposed
C-21	880	0.1423	25.37	4.36	43.81	6.16	48.48	1.55
C-20	900	0.1676	24.82	3.58	42.85	5.06	50.54	1.55
C-22	950	0.1487	21.59	2.96	37.27	4.18	58.55	0
C-24	950	0.1332	21.25	2.78	36.69	3.93	59.38	0
C-3	* 950	0.1328	24.92	3.61	43.04	5.10	51.86	0
C-2	* 950	0.1154	25.41	3.47	43.87	4.91	51.22	0

* The cracking Pt-silica gel catalyst was inserted in the reaction tube as shown in Fig. 6-A, the other as in Fig. 6-B.



×: The position, at which the temperature was measured.

Fig. 6. Modes of Charging Pt-silica Gel Catalyst.

In the previous paper the percentage decompositions of oxygen of saccharose as a function of cracking temperatures were ascertained, and, therefore, percentage of carbon monoxide and that of oxygen remained undecomposed may be calculated, combining with the data here obtained.

The results of Table 4 show that the oxygen of saccharose is largely decomposed into water vapour and carbon monoxide, and the higher the cracking temperature, the more carbon monoxide and the less water vapour and carbon dioxide are produced. The different results of C-2, C-3 from those of C-22, and C-24 are easily explained through the different temperature distributions of cracking catalyst.

(3) *Influence of Streaming Velocity of Hydrogen.* The cracking catalyst was inserted as shown in Fig. 6-B and the influence of streaming velocity of hydrogen was examined and the results obtained were shown in Table 5.

Table 5. The influence of streaming velocity of hydrogen.

Sample saccharose, temp. of Pt-silica gel catalyst 950°C., analytical period 60 min..

Expt. No.	H_2 Vel. l./hr.	Sample g.	H_2O produced %	CO_2 produced %	CO (diff.) %	Oxygen balance		
						to H_2O	to CO_2	to CO
C-27	2.2	0.1641	22.48	4.20	28.09	38.81	5.93	55.26
C-25	3.0	0.1423	21.64	3.51	29.64	37.37	4.96	57.67
C-24	4.0	0.1332	21.25	2.78	30.52	36.69	3.93	59.38
C-28	4.8	0.1391	22.14	1.94	30.34	38.23	2.74	59.03

The rapid flow of hydrogen produced the decreased production of carbon dioxide and the increased production of carbon monoxide, while the amount of water approximately remaining constant.

(4) *Cracking of Other Several Organic Compounds.* Succinic acid, benzoic acid, and anthraquinone were examined for their cracking behaviour in the same way as in the case of saccharose. The results of Table 6 indicate that the sample which contained large amount of oxygen tends to give large amount of carbon dioxide, particularly at lower temperatures.

Table 6. The cracking of several organic compounds at various temperature.

Streaming velocity of H_2 4 l./hr., analytical period 60 min..

Expt. No.	Sample	Temp. of Pt-silica gel Catalyst °C.	Sample g.	H_2O produced %	CO_2 produced %	Oxygen balance		
						to H_2O	to CO_2	to CO
C-40	Succinic acid (0%=54.22)	850	0.1405	15.94	18.93	26.11	25.40	—
C-41		860	0.2274	12.01	17.15	19.67	23.00	—
C-39		900	0.1809	10.17	10.06	16.65	13.50	—
C-38		950	0.1828	6.35	3.83	10.40	5.15	84.45
C 36	Benzoic acid (0%=26.22)	800	0.1213	0.99	1.32	3.36	3.36	—
C-34		850	0.1240	0.56	1.29	1.90	3.55	—
C-35		900	0.1492	0.47	1.00	1.60	2.78	—
C-33		950	0.1317	0.30	0.68	1.03	1.87	97.10
C-42	Anthraquinone (0%=15.37)	950	0.2757	0.22	0.22	1.27	1.04	97.69

(5) Discussion of Results. *Calculation of Oxygen Distribution Balance.* At the high temperatures as 800~950°C. all the organic compounds containing oxygen decompose and liberate their oxygen as carbon monoxide, carbon dioxide, and water vapour, and, therefore, the following several reactions have to be considered in the discussion of the results.

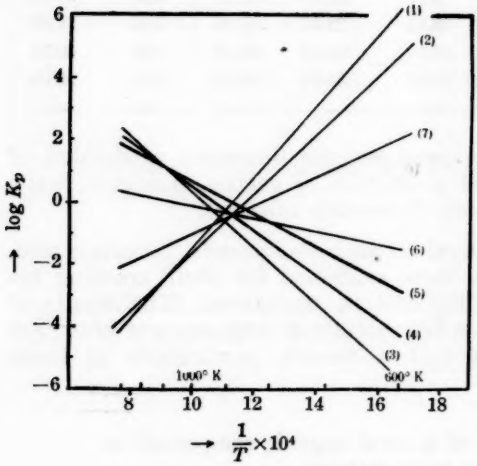
$$C + CO_2 \rightleftharpoons 2CO \quad \cdots\cdots (3)$$

$$C + H_2O = CO + H_2 \quad \cdots\cdots (4)$$

$$C + 2H_2O = CO_2 + 2H_2 \quad \cdots\cdots (5)$$

$$CO_2 + H_2 = CO + H_2O \quad \cdots\cdots (6)$$

$$C + 2H_2 = CH_4 \quad \cdots\cdots (7)$$



(1) $CO + 3H_2 = CH_4 + H_2O$
(2) $CO_2 + 4H_2 = CH_4 + 2H_2O$
(3) $C + CO_2 = 2CO$
(4) $C + H_2O = CO + H_2$
(5) $C + 2H_2O = CO_2 + 2H_2$
(6) $CO_2 + H_2 = CO + H_2O$
(7) $C + 2H_2 = CH_4$

Fig. 7. Relation between Equilibrium Constants and Reaction Temperatures.

The dependence of equilibrium constants Kp on the temperatures of these reactions are represented in Fig. 7. Reaction (5) is the combination of reaction (4) and (6) and is not necessary to be considered here. The Kp of reaction (3), (4), and (6) increase with temperature and, therefore, produce more carbon monoxide. The percentage distributions of oxygen in the products of reactions are calculated and plotted in Fig. 8–11 as a function of temperatures.

The reaction (3) occurs under approximately 1/10 atmosphere in our analytical conditions and consequently ought to give at equilibrium about 1% of carbon dioxide at 950°C. (Fig. 8). H_2/CO_2 being 10~20, the reaction (6) may produce 3–6% of

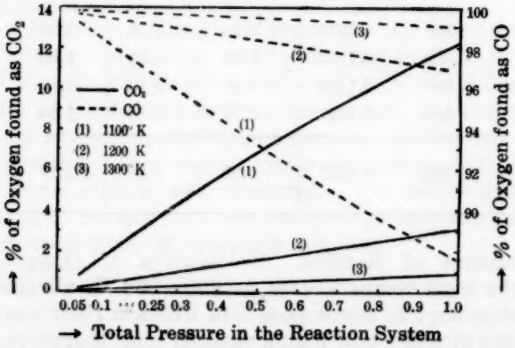

% of Oxygen found as CO2
% of Oxygen found as CO
CO2
CO
(1) 1100° K
(2) 1200 K
(3) 1300° K
0.05 0.1 0.25 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Total Pressure in the Reaction System

Fig. 8. Oxygen Balance in $C+CO_2 = 2CO$.

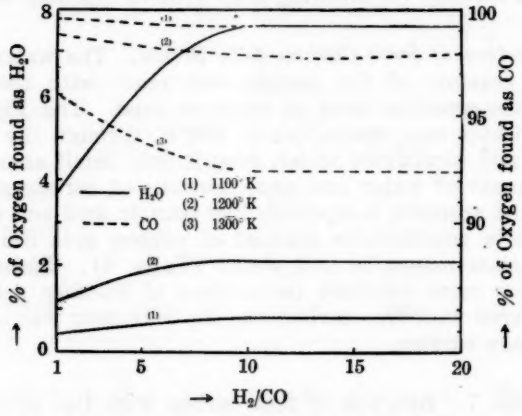


Fig. 9. Oxygen Balance in $C+H_2O=CO+H_2$.

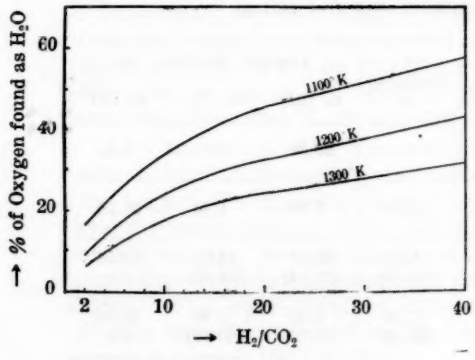


Fig. 10. Oxygen Balance in $C+2H_2O=CO_2+2H_2$

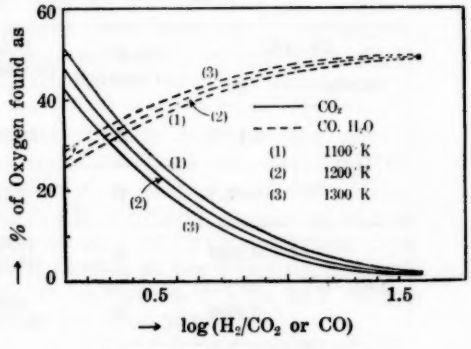


Fig. 11. Oxygen Balance in $CO_2+H_2=CO+H_2O$.

carbon dioxide at 950°C. and the large proportion of oxygen in the sample will appear as carbon monoxide and water vapour. These estimations are quite concordant with our experimental results.

(6) *Reaction of Free Carbon with Carbon Dioxide.* The aromatic compounds produce on decomposition quite considerable amount of free carbon. The increase of streaming velocity of hydrogen reduces the mean partial pressures of carbon oxide and, therefore, drive the equilibrium point of reaction (3) toward the carbon monoxide side and reduces the carbon dioxide formation. On the contrary the decrease of hydrogen velocity favours the carbon dioxide formation. These considerations show good agreement with the experimental results given in Table 5. Succinic acid and saccharose give at 950°C. 3–4% of carbon dioxide and these are more than the equilibrium figures and, therefore, it is concluded that the cracked gases from the compounds which contain large amount

of oxygen pass through the cracking zone without reaching the equilibrium point.

(7) *Reaction of Free Carbon with Steam.* The water produced by the cracking reaction of the sample will react with the free carbon deposited in the cracking zone of reaction tube. The Fig. 9 indicates that 97% of water may decompose at 950°C. through the reaction (4). Succinic acid and saccharose which deposit only small amount of carbon give large amount of water and small amount of carbon monoxide. On the contrary the aromatic compounds like benzoic acid and anthraquinone which produce a considerable amount of carbon give nearly calculated amount of carbon monoxide and water (Table 6). Planning to prove these conclusion more definitely the surface of Pt-silica gel catalyst was purposely covered with free carbon and its behaviour was compared with that of the clean surface.

Table 7. Reaction of free carbon with H_2O or CO_2

Temp. of Pt-silica gel catalyst 950°C., H_2 velocity 4 l./hr.,
A cases, the catalyst was clean
B cases, the catalyst was covered with free carbon

Sample		Condition of catalyst	H_2O produced %	CO_2 produced %	Oxygen balance, %		
Kinds	g.				to H_2O	to CO_2	to CO
H_2O	0.1441	A	99.39	0	99.39	0	0.61
	0.0428	B	2.10	1.64	2.10	1.34	96.56
$NaHCO_3$*	0.2830	A	16.86 (10.72)	5.90 (26.19)	52.41 (33.34)	15.01 (66.66)	32.58 (0)
	0.2199	B	0.79 (10.72)	0.79 (26.19)	2.46 (33.34)	1.99 (69.66)	95.55 (0)

* The sample bicarbonate, on heating to 300°C. decomposed stoichiometrically, $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$, and gave the products of figures in brackets.

The results of Table 7 prove quite conclusively the deduction discussed above. These data, furthermore, indicate that the presence of sufficient amount of free carbon produces the equilibrium mixture of cracked gases after the reaction (4).

(8) *Water-gas Reaction.* In order to decide whether the reaction (6) participates or not in the formation of water in the cracking zone, the behaviour of sodium oxalate which produces only carbon monoxide and carbon dioxide and no water was examined and the results obtained were given in Table 8. The degree of decomposition of sodium oxalate at 950°C. was found to be about 90.0% by the blank experiments. It is clear that the reaction (6) is also responsible for the formation of water and also that the reaction (6) does not reach the equilibrium point of these cases in which the initial concentration of carbon dioxide is exceedingly high.

Table 8. Cracking of sodium oxalate.

$$Na_2C_2O_4 = Na_2O + CO_2 + CO$$

Expt. No.	Sample g.	Temp. of Pt-silica gel catalyst °C.	H_2 Vel. l./hr.	Oxygen balance, %		
				to H_2O	to CO_2	to CO (diff.)
C-53	0.2037	800	3.8	27.66	21.68	50.66
C-52	0.2901	900	3.0	22.53	21.28	56.19
C-51	0.3183	950	4.0	22.93	19.56	57.51
C-50	0.2654	1000	3.5	22.44	10.41	67.15

(9) *Reaction of Free Carbon with Hydrogen.* The free carbon produced in the cracking zone may combine with hydrogen and disappear as methane; however, at such a high temperature as 950°C. the equilibrium of reaction (7) is unfavorable for the production of methane and, furthermore, the free carbon formed may be transformed into a stable form and loses its activity toward hydrogen; thus resulting in the accumulation of free carbon on Pt-silica gel catalyst in the cracking zone. It is, therefore, necessary to burn off the free carbon with air from time to time, usually after 7–10 analyses.

In conclusion, the mechanism of reaction in the cracking zone is satisfactorily explained by the occurrence of reactions (3), (4), and (6); the higher the cracking temperature the more carbon monoxide forms, and the rapid heating of the sample in the boat or high content of oxygen of the sample favours the increasing amount of carbon dioxide, thus exceeding equilibrium amount of carbon dioxide at the cracking temperatures. The mechanism of reduction of carbon monoxide and carbon dioxide thus formed will be discussed in the next paper.

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The Formation of Polyhydroxy-dialdehydes. I. Xylo-trihydroxy-glutaric Dialdehyde and its Derivatives.

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Among the onoses, namely, sugars which have two carbonyl groups in separated positions, those with one aldehydic and one ketonic groups have been reported by some investigators.[1] While, very little is known about the onoses with two aldehydic groups;[2] and nothing seems to have been reported about dialdo-pentonoses, that is, trihydroxy-glutaric dialdehydes, where it should exist theoretically four such dialdehydes. So attempts were made to obtain these series of sugars, and xylo-trihydroxy-glutaric dialdehyde and *d*-lyxo-trihydroxy-glutaric dialdehyde (xylo- and lyxo-dialdo-pentonose) and their derivatives were now prepared.[3] This communication concerns with the formation of xylo-derivatives.

For this purpose, 1,2-monoacetone-*d*-glucofuranose is oxidized by lead tetracetate[4] in benzene solution. The mixture is filtered, the filtrate evaporated under diminished pressure, and 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde is obtained by distilling the remaining sirup. It distils at 132°–136° in 0.01–0.02 mm pressure. It is a colourless hygroscopic sirup, although it can be made powdery. It is not sweet, but bitter. $[\alpha]_D^{16} = 20° \pm 3°$.

The phenylhydrazone of 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde is prepared by boiling the alcoholic solution of dialdehyde with phenylhydrazine. It is recrystallized first from the mixture of benzene and petroleum ether and then from dilute alcohol. It crystallizes in colourless needles or leaflets. Melting point, 140.5°–141° (corrected). $[\alpha]_D^{19} = -41° \pm 1°$ in chloroform.

The semicarbazone of 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde is prepared by adding semicarbazide hydrochloride and potassium acetate to the aqueous solution of the acetone derivative. It crystallizes in fine colourless leaflets. The melting point is 209°–209.5° (corrected, decomposing).

Xylo-trihydroxy-glutaric dialdehyde is obtained by hydrolizing the above acetone-derivative with 1% sulphuric acid in a boiling water bath. It does not crystallize, but its *bis*-phenylhydrazone and *bis*-*p*-nitrophenylhydrazone are obtained crystalline by adding phenylhydrazine or *p*-nitrophenylhydrazine to the acidic solution of xylo-trihydroxy-glutaric dialdehyde. Melting point of *bis*-phenylhydrazone of xylo-trihydroxy-

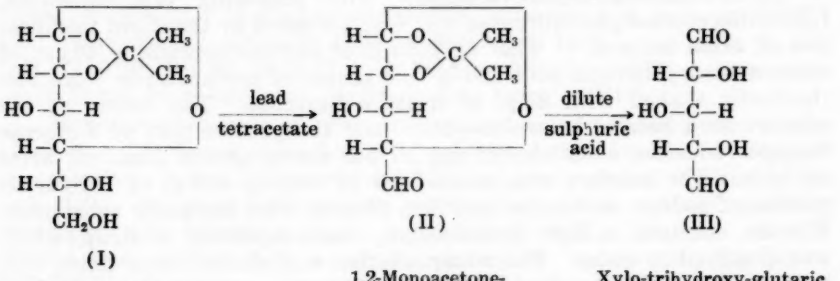
(1) For instance: B. Helferich and E. Himmen, *Ber.*, **62** (1929), 2136; B. Helferich and N. M. Bigelow, *Z. physiol. Chem.*, **200** (1931), 263.

(2) H. O. L. Fischer and H. Appel, *Helv. Chim. Acta*, **17** (1934), 1574.

(3) The author reported on these on the annual meeting of the Chemical Society of Japan in July 1940 at Sapporo.

(4) Criegee, *Ann.* **507** (1933), 159.

glutaric dialdehyde is 126.5°–127.5° (corrected), and that of its *bis-p*-nitrophenylhydrazone is 191°–192° (corrected, decomposing).



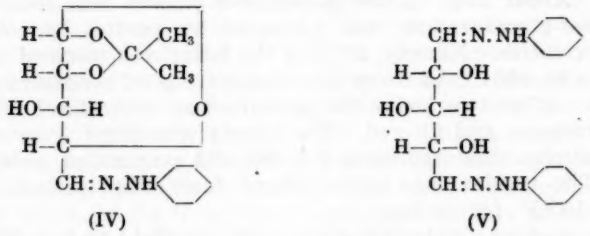
(I) (II) (III)

1,2-Monoacetone-*d*-glucofuranose

1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde

Xylo-trihydroxy-glutaric dialdehyde (described arbitrarily in chain formula)

Phenylhydrazine Phenylhydrazine

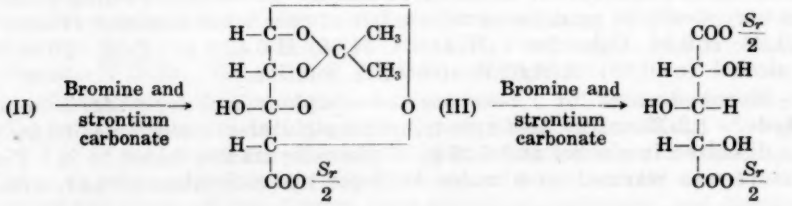


(IV) (V)

1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde monophenylhydrazone

Xylo-trihydroxy-glutaric dialdehyde *bis*-phenylhydrazone (described arbitrarily in chain formula)

By oxidizing the aldehyde groups of such dialdehyde derivatives with bromine, the corresponding carboxylic acids are obtained. Thus, strontium salt of 1,2-monoacetone-*d*-xyluronic acid is obtained by oxidizing 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde with bromine, generated acids being neutralized by excess of strontium carbonate. And, by the same method, strontium salt of xylo-trihydroxy-glutaric acid is obtained from xylo-trihydroxy-glutaric dialdehyde.



Strontium 1,2-monoacetone-*d*-xyluronate

Strontium trihydroxy-glutarate

Experimental.

1,2-Monoacetone-d-glucofuranose. For preparing this substance, 1,2,5,6-diacetone-*d*-glucofuranose was first prepared by the slight modification of usual method.[5] That is, 700 c.c. of acetone containing 40 c.c. of concentrated sulphuric acid and a few grams of acetaldehyde were mechanically shaked with 35 g. of usual *α*-*d*-glucose. The colour of the mixture soon became brownish-yellow, and the greater part of *d*-glucose disappeared after a half hour, and all but coarse grains dissolved after an hour. The mixture was neutralized by adding 150 g. of anhydrous powder of sodium carbonate, and then filtered from inorganic substances. Filtrate, coloured in light lemon-yellow, was evaporated to sirup, which was dissolved in water. The water solution was shaked three times with benzene to remove resinous material, benzene extract thus obtained washed twice with water, and combined water solution was extracted six times with each 100 c.c. of chloroform. Chloroform extract, containing diacetone-*d*-glucose, was dried with anhydrous sodium sulphate, and evaporated. About 25 g. of raw diacetone-*d*-glucose was obtained. 1,2-Monoacetone-*d*-glucofuranose was prepared by partial hydrolysis[6] of diacetone derivative. Namely, 20 g. of the latter was warmed in a water bath at 50° with 400 c.c. of water containing 0.8 g. of concentrated hydrochloric acid. After two hours the mixture was neutralized with excess of silver carbonate, and filtered. The filtrate was freed from silver ions by passing sulphuretted hydrogen, filtered, and evaporated under reduced pressure. The residue was recrystallized from ethyl acetate. Melting point. 160–160.5° (corrected).

1,2-Monoacetone-d-xylo-trihydroxy-glutaric dialdehyde. Ten grams of lead tetracetate were dissolved in 200 c.c. of benzene. To this, 5 g. of monoacetone-glucose were added, and the mixture was shaked and warmed in a water bath for a few minutes. After standing for a short while, the cooled mixture was filtered and the residue was thoroughly washed with 200 c.c. of acetone. Combined filtrate and washings were evaporated under reduced pressure, the temperature of the bath not being allowed to rise above 40°. The thick sirup thus obtained was dissolved in alcohol, filtered and again evaporated in vacuo. This procedure was twice repeated. The remaining sirup was now dissolved in ether, filtered from insoluble material and the solvent was removed under diminished pressure. This sirup was distilled in high vacuum. Boiling point, 132–136° at 0.01–0.02 mm. pressure. It is a colourless, glassy and very thick sirup which can be made powdery. It is also hygroscopic. It reduces Fehling's solution very slowly at room temperature, but at once when heated. (Found: C 51.26, H 6.80. Calc. for $C_8H_{12}O_5$: C 51.06, H 6.43%). $[\alpha]_D^{16}=20°\pm3°$ in alcohol (c=0.65) thirty minutes after solution.

Monohydrazone of 1,2-monoacetone-d-xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was dissolved in alcohol and 0.25 g. of phenylhydrazine added to it. The mixture was warmed on a water bath for about 5 minutes, and, after

(5) K. Freudenberg and K. Smeykal, *Ber.*, **59** (1926), 100; *Ber.*, **61** (1928), 1741.
(6) E. Fischer, *Ber.*, **28** (1895), 2496.

cooling, poured into water. The separated oil solidified on standing. It was recrystallized first from the mixture of benzene and petroleum ether, and then twice from dilute alcohol (the mixture of 2 parts of water and 1 part of alcohol). It is colourless needles or leaflets. It melts at 140.5°–141° (corrected). (Found: C 60.74, H 6.39, N 10.15. Calc. for $C_{14}H_{18}O_4N_2$: C 60.42, H 6.52, N 10.07%). $[\alpha]_D^{19} = -41° \pm 1°$ (0.2071 g. was made up to 10 c.c. by chloroform, direct reading being –0.84°).

Monosemicarbazone of 1,2-monoacetone-d-xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.2 g.) was dissolved in 4 c.c. of water, and 0.2 g. of semicarbazide hydrochloride and 0.3 g. of potassium acetate were added to it. After standing overnight, fine colourless leaflet separated from the solution. It was filtered and washed with a small quantity of water. Melting point, 209–209.5° (corrected, decomposing). (Found: N 17.21. Calc. for $C_9H_{15}O_5N_3$: N 17.14%).

Xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was dissolved in 30 c.c. of 0.1 N sulphuric acid and heated in a boiling water bath for an hour. The solution was neutralized with excess of barium carbonate, small quantity of active charcoal added, and the mixture was filtered. Dialdehyde was obtained as sirup by evaporating the filtrate under reduced pressure. It reduces Fehling's solution after several minutes at room temperature, but at once reduces it strongly when heated.

Bis-phenylhydrazone of xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was hydrolized with 30 c.c. of 0.1 N sulphuric acid, and to this mixture 0.5 g. of phenylhydrazine was added. The separated mobile oil was washed with the mixture of benzene and petroleum ether, and the residual oil solidified after standing overnight. It was partly dissolved in a very small quantity of acetone, and then petroleum ether was added to this mixture. The precipitated *bis*-phenylhydrazone was recrystallized from alcohol. It melts at 126.5°–127.5° (corrected). It is colourless leaflet. (Found: C 62.05, H 6.53, N 16.86. Calc. for $C_{17}H_{20}O_3N_4$: C 62.18, H 6.17, N 17.06%).

Bis-p-nitro-phenylhydrazone of xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was hydrolized with 30 c.c. of 0.1 N sulphuric acid, and to this mixture 0.8 g. of *p*-nitro-phenylhydrazine dissolved in dilute sulphuric acid was added. *Bis-p*-nitro-phenylhydrazone precipitated at once from the mixture. It was filtered and washed with water. And the precipitate was recrystallized from pyridine. Yellow needles. It is slightly soluble in alcohol, more in acetone. It melts at 191–192° (corrected, decomposing). (Found: N 19.82. Calc. for $C_{17}H_{18}O_7N_6$: N 20.09%).

Strontium 1,2-monoacetone-d-xyluronate. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (1 g.) was dissolved in 50 c.c. of water and 8 g. of strontium carbonate and 1.5 g. of bromine were added to it. The mixture was frequently shaked for several hours and then kept standing for two days. It was filtered from strontium carbonate, and dissolved bromine was removed by airing under reduced pressure. Then the solution was stirred on adding silver carbonate to remove bromine ions and

filtered. Sulphuretted hydrogen was passed in the filtrate to eliminate silver ion and the mixture was again filtered. When the filtrate was evaporated under reduced pressure to a small volume, a considerable quantity of white precipitate appeared. Then the concentration was stopped, and alcohol was added to it. The mixture was filtered after standing for a short while. Strontium 1,2-monoacetone-*d*-xyluronate thus obtained is white crystalline powder and is slightly soluble in water. (Found: C 38.41, H 4.63, Sr 17.99. Calc. for $C_{16}H_{22}O_{12}Sr$: C 38.91, H 4.46, Sr 17.75%).

Strontium xylo-trihydroxy-glutarate. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was hydrolized with 30 c.c. of 0.1 N sulphuric acid and to this mixture 5 g. of strontium carbonate and 1.6 g. of bromine were added. After standing overnight it was filtered and the filtrate was treated just like above mentioned method for strontium 1,2-monoacetone-*d*-xyluronate. Strontium xylo-trihydroxy-glutarate is slightly soluble in water. (Found: Sr 33.46. Calc. for $C_5H_6O_7Sr$: Sr 32.98%).

Summary.

By the oxidation of 1,2-monoacetone-*d*-glucofuranose with lead tetraacetate, 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde was obtained, which distils at 132–136° at 0.01–0.02 mm. pressure, and has specific rotatory power, $[\alpha]_D^{16}$, of 20°±3° in alcohol. Its monophenylhydrazone melts at 140.5–141° and has specific rotatory power, $[\alpha]_D^{19}$, of –41°±1° in chloroform, and its monosemicarbazone melts at 209.5°. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde was hydrolized to xylo-trihydroxy-glutaric dialdehyde and *bis*-phenylhydrazone and *bis*-*p*-nitrophenyl-hydrazone of the latter were obtained. Melting points of them are 126.5–127.5° and 191–192° respectively. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde and xylo-trihydroxy-glutaric dialdehyde were oxidized by bromine in presence of strontium carbonate, and strontium 1,2-monoacetone-*d*-xyluronate and strontium xylo-trihydroxy-glutarate were obtained respectively.

In conclusion the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

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Polymerisation of Tung Oil. V. Effects of Treated Fatty Oils upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

As the nature of fatty oil is markedly affected by various treatments, the effect of several kinds of fatty oil treated by different ways upon the gelation time of tung oil is dealt in the present paper.

Cooked drying oils. Drying oils such as linseed or perilla oils are usually cooked and at the end of cooking they turn by oxidation or polymerisation into a gelatinous state, therefore the gelation preventing action of these oils upon tung oil should be affected by their cooking degree. To obtain the relation between x_∞ and the cooking degree, the following experiments were done. The measurements of gelation times carried out at 270°C. were the same as in the previous report.

I. Oxidised and polymerised linseed oils. The cooked oils were obtained by oxidising linseed oil at 100°C. with oxygen, and by polymerising it at 287°C. in carbon dioxide atmosphere.

Table 1. Raw linseed oil.

(iodine value 172.4).

x (%)	t (270°C.)	t (280°C.)
10.40	1040	730
20.00	1228	841
30.15	1576	1075
x_∞	67%	66%

Table 2. Oxidised linseed oil No. 1.

(iodine value 140.8).

x (%)	t (270°C.)	t (280°C.)
10.22	989	691
20.21	1167	828
30.86	1367	950
x_∞	85%	86%

Table 3. Oxidised linseed oil No. 2.

(iodine value 124.1).

x (%)	t (270°C.)	t (280°C.)
10.40	944	688
20.71	1036	751
30.97	1165	843
x_∞	122%	122%

Table 4. Oxidised linseed oil No. 3.

(iodine value 115.9).

x (%)	t (270°C.)	t (280°C.)
15.0	971	719
30.6	1068	798
x_∞	196%	198%

Table 5. Polymerised linseed oil No. 1.

(iodine value 161.0).

x (%)	t (270°C.)
0	882
5.23	942
15.1	1106
30.9	1595
x_∞	69%

Table 6. Polymerised linseed oil No. 2.

(iodine value 140.3).

x (%)	t (270°C.)
7.73	947
10.00	1010
15.00	1067
30.00	1430
x_∞	73%

Table 7. Polymerised linseed oil No. 3.

(iodine value 124.1),

x (%)	t (270°C.)
10.58	985
20.55	1146
29.28	1230
x_∞	87%

Table 8. Polymerised linseed oil No. 4.

(iodine value 122.2).

x (%)	t (270°C.)
15.04	1085
30.40	1435
x_∞	88%

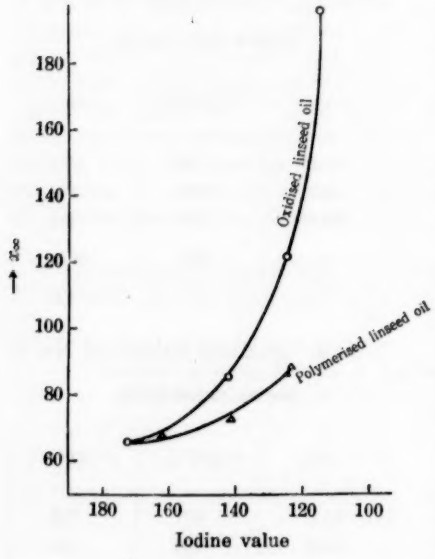

Fig. 1.

The relation of x_∞ to the iodine value of cooked oils is shown in Fig. 1.

From Fig. 1 it is noticed that the value of x_∞ increases with the increase of cooking degree; that is, the gelation-preventing action becomes weaker, as the cooked oil itself has the gelation tendency.

For the same cooking degree, the value of x_∞ for the oxidised linseed oil is greater than that for the polymerised oil. This coincides with the fact that the drying power of oxidised oil is always greater than that of polymerised oil[1].

II. Oxidised perilla oil. The gelation retarding effect of the oxidised perilla oils oxidised at 100°C., 200°C. and 300°C. was measured.

(1) M. Tatimori, *Hitachi Hyoron*, **20** (1937), 43.

Perilla oil taken in 1l. beaker were oxidised, by air-blowing at temperatures of 100°C., 200°C. and 300°C. respectively. The oxidised oils then had the following constants.

Table 9.

Kind of oil		Abbreviation	Iodine value
Raw Perilla oil		200 (0)	210.0
Oxidised at	100°C.	170 (100)	175.5
,,	200°C.	170 (200)	177.6
,,	300°C.	170 (300)	177.5
,,	100°C.	150 (100)	160.4
,,	200°C.	150 (200)	156.5
,,	300°C.	150 (300)	149.9
,,	100 C.	140 (100)	140.7
,,	200 C.	140 (200)	140.9
,,	300 C.	140 (300)	137.5

Table 10.

Kind of oil and Remarks	Amount of addition (x %)	Gelation time (t, sec.)	Kind of oil and Remarks	Amount of addition (x %)	Gelation time (t, sec.)
200 (0): The relation between $1/t$ and x is linear and the value of x_∞ becomes 59.5%.	0	881	150 (200): A curved line is obtained, the estimated value of x_∞ is 84%.	0	885
	10	1040		10	950
	20	1254		20	1050
	30	1622		30	1184
	40	2338		40	1375
	50	3899		50	1590
170 (100): The relation of $1/t$ and x forms a convex curve, the estimated value of x_∞ is 62%.	0	888	150 (300): A straight line is obtained, x_∞ is 89%.	0	870
	10	1017		10	980
	20	1140		20	1120
	30	1409		30	1269
	40	1794		40	1498
	50	2695		50	1777
170 (200): The relation of $1/t$ and x forms nearly a straight line and x_∞ is 66%.	0	884	140 (100): A curved line is obtained.	0	886
	10	1057		10	899
	20	1170		20	940
	30	1524		30	982
	40	1935		40	1018
	50	2842		50	1086
170 (300): The relation between $1/t$ and x is linear and x_∞ is 66%.	0	885	140 (200):	0	884
	10	1144		10	910
	20	1348		20	983
	30	1660		30	1074
	40	2197		40	1177
	50	3130		50	1298
150 (100): A curved line is obtained, the estimated value of x_∞ is 67%.	0	886	140 (300): The relation between $1/t$ and x is linear and x_∞ is 110%.	0	884
	10	942		10	930
	20	1032		20	1018
	30	1200		30	1101
	40	1464		40	1255
	50	2040		50	1422
				100	5012

The relations between the reciprocals of gelation times and the amount of addition of oils are shown in Fig. 2.

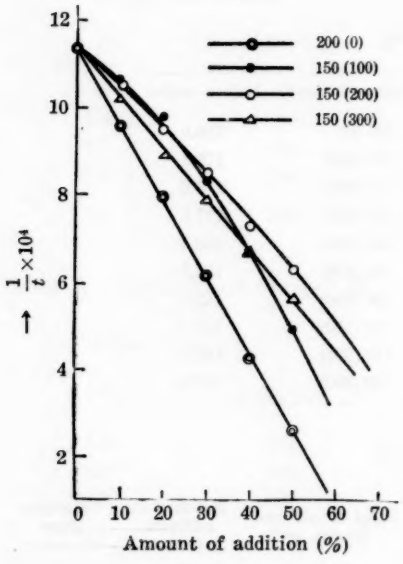

Fig. 2.

From the above rsults it is concluded that with the addition of oxidised oils at 300°C. the relation of $1/t$ and x are linear, on the contrary in the cases of oxidised oils at 100°C. curved lines are obtained and in the cases of oxidised oils at 200°C., those of the beginning of cooking, a straight line, but those of the increased degree of cooking curved lines are obtained.

It is supposed that oxidised fatty oil prepared at low temperature contains a substance which has special action upon the gelation of tung oil. M. Nakamura[2] reported that oxidised fatty oil prepared at temperatures lower than 160°C. contains a peroxide, while high temperature oxidation oil does not contain it. The author conformed from a qualitative experiment that the oil oxidised at 100°C. contains peroxide, while that oil oxidised at 300°C. does not contain it.

Therefore the curved nature of the relation between $1/t$ and x is supposed to be due to the peroxide contained in the oil.

III. Effect of benzoyl peroxide. To verify the above presumption the effect of benzoyl peroxide were studied.

Table 11. Effect of perilla oil added with 5% of benzoyl peroxide.

x (%)	t (sec.)
0	885
10	1032
20	1168
30	1512
40	2111
50	3762

Table 12. Effect of perilla oil added with 10% of benzoyl peroxide.

x (%)	t (sec.)
0	878
10	981
20	1125
30	1353
40	1775
50	2911

(2) *J. Chem. Ind. Japan*, **40** (1937), 448.

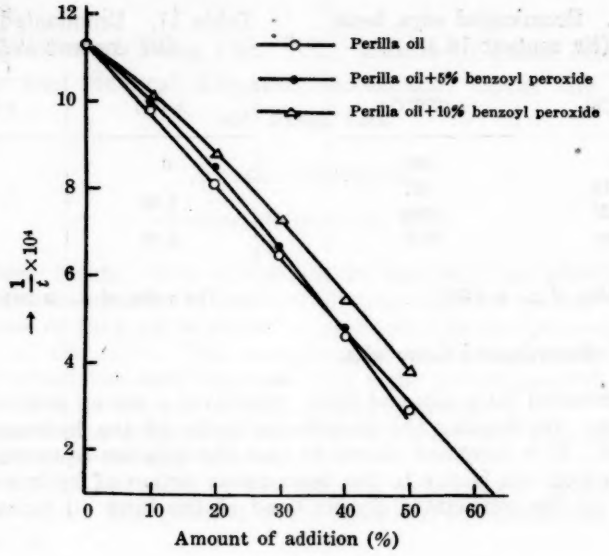

Fig. 3.

The nature of the curve is similar to that of oxidised perilla oil prepared at 100°C.

From the above results benzoyl peroxide has a great accelerating action upon the gelation of tung oil. It is a well known fact that peroxides have accelerating actions upon the polymerisation of butadiene and styrol. It is concluded that the curved nature of $1/t$–x relation of oxidised perilla oil is due to the superposed effects of retarding action of oxidised perilla oil and of accelerating action of peroxide contained in it. The relation of x_∞ to the degree of cooking of oxidised oil prepared at 300°C. is shown in Table 14.

Table 13.

Effect of benzoyl peroxide.

x (%)	t (sec.)
0	883
0.1	860
0.3	837
0.5	810
0.8	760
1.0	730
10.0	349
20.0	148
30.0	23

Table 14.

Kind of oil	x_∞ (%)	Iodine value
200 (0)	59.5	210.0
170 (300)	66.0	177.5
150 (300)	89.0	149.9
140 (300)	110.0	137.5

The value of x_∞ increases according to the increase of cooking degree. This tendency is similar to that of the cooked linseed oil.

Table 15. Brominated soya bean oil (Br content 31.3%).

x (%)	t (270°C.)
0	904
1.09	885
2.07	958
3.00	1410

The gelation preventing action is very strong and the value of x_∞ is less than 6%.

Table 16. Brominated soya bean oil (Br content 16.4%)

x (%)	t (270°C.)
0	903
1.19	791
2.27	1088
3.00	3818

The value of x_∞ is 3.5%.

Table 17. Brominated oleic acid (Br content 17.7%).

x (%)	t (270°C.)
0	1086
1.43	1291
2.00	1994

The value of x_∞ is less than 3.0%.

IV. Brominated fatty oils.

Brominated fatty oils and fatty acids have a strong gelation—retarding action. On heating the brominated fatty oil the hydrogen bromide is evolved. It is supposed therefore that the gelation—preventing action of brominated oils is due to the isomerizing action of hydrogen bromide exerting on the conjugated double bond of the tung oil molecule.

Summary.

1. The gelation—preventing actions of oxidised and polymerised linseed oil were measured. The value of x_∞ increases with the increasing degree of cooking and the value for oxidised oils is always greater than that for polymerised oils of the same cooking degree.

2. Perilla oil was oxidised at 100°C., 200°C. and 300°C. to the degrees of iodine values 170, 150, 140 and the effects upon the gelation were measured. In the cases of oxidised oil prepared at 300°C. the relation of $1/t \sim x$ was linear and the value of x_∞ increase according to the increase of cooking degree. In the cases of oxidised at 100°C. and 200°C. curved lines were obtained. This tendency is supposed to be due to the peroxide contained in it.

3. The effect of benzoyl peroxide also was examined. Benzoyl peroxide has a strong gelation accelerating action. The effect of perilla oil added with benzoyl peroxide is similar to that of perilla oil oxidised at low temperature.

4. The gelation—preventing action of brominated oils is very strong and the value of x_∞ is less than 4%. Therefore, these substances can be used as a strong gelation—preventing agent.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota, for their kind guidance.

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Polymerisation of Tung Oil. VI. Effects of Fatty Acids, Fatty Alcohols and Several Organic Substances upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

I. Fatty Acids. It is a well known fact that the addition of any acidic substance retards the gelation of tung oil when cooked[1], and the gelation time of tung oil increases in proportion to the increasing degree of acidity of the oil[2]. The interpretation of the mechanism for this retarding action has been attempted by some investigators[3], but it is likely that there is not yet a definite theory hereabout.

The measuring methods of the gelation time etc. were the same as those described in the previous report.

(1) *Simple fatty acids.* The Merck's pure stearic, oleic and linolic acids were used. The gelation times measured in second are shown in Table 1 and 2.

Table 1.

	Temp. (°C.)	0%	5%	7.5%	10.0%	12.5%	15.0%
Stearic acid	260	1386	1626	—	1957	—	—
	270	940	1115	1250	1397	1501	1768
	280	682	819	928	1053	1199	1482
Linolic acid	260	1340	1526	—	1769	1959	2226
	270	937	1068	1160	1262	1380	1592
	280	682	782	869	956	1050	1334

Table 2. Oleic acid.

Temp. (°C.)	0%	5%	7.5%	10.0%	12.5%	15.0%	20.0%
320	282	378	—	1560	—	—	—
310	349	475	—	781	—	4980	—
300	405	520	580	722	1130	2988	—
290	532	643	—	830	—	1482	—
280	702	834	908	1036	1192	1476	9720
270	961	1132	1207	1327	1765	1892	2820
260	1320	1575	1727	1911	2132	2369	3588
250	1995	2253	—	2699	—	3420	—

(1) R. Bürstinbinder, *Farben Ztg.*, **23** (1917), 243; H. Rhodes, J. Potts, *Chem. Metall. Eng.*, **29** (1923), 533.
(2) H. A. Gardner, *Chem. Absts.*, **15** (1921), 1081.
(3) Krumbhaar, *ibid.*, **9** (1915), 2155; L. A. Jordan, *J. Chem. Ind.*, **53** (1934), 1.

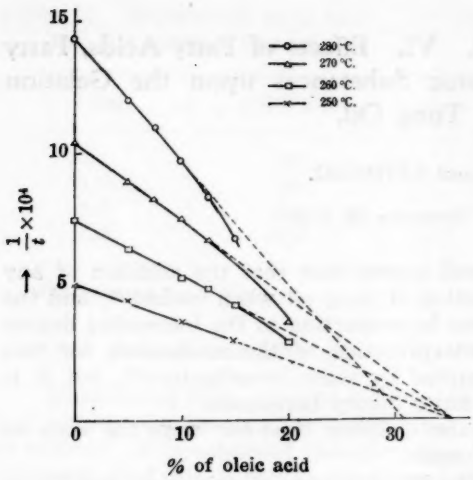

Fig. 1.

The relations between the reciprocals of gelation time ($1/t$) and the percentage of oleic acid (x) present are shown in Fig. 1.

(2) *Mixed fatty acids.* The fatty acids of tung, linseed, soyabean and sesame oils were prepared by the saponification of the respective oils by the usual methods. The gelation times are shown in the following tables.

Table 3. Tung oil acids.

Temp. (°C.)	6.9%	9.8%	14.4%	19.8%
270	1046	1150	1318	1570
280	730	808	945	1151

Table 4. Linseed oil acids.

Temp. (°C.)	5.07%	10.2%	15.0%	20.2%
270	1016	1196	1466	1948
280	726	884	1121	1677

Table 5. Soya bean oil acids.

Temp. (°C.)	5.09%	10.1%	14.7%	19.6%
270	1062	1278	1578	1771
280	775	938	1236	2269

Table 6. Sesame oil acids.

Temp. (°C.)	5.0%	10.9%	15.0%	20.3%
270	1152	1482	1764	2601
280	801	1063	1427	2361

The linear relations exist between $1/t$ and x, when x is less than 15%, beyond which curved lines are obtained. The values of x_∞ can be

Table 7. x_∞ (at 270°C.)

Stearic acid	32.0%
Oleic acid	33.5
Linolic acid	38.0
Fatty acids of sesame oil	33.3
Fatty acids of soya bean oil	34.0
Fatty acids of linseed oil	35.0
Fatty acids of tung oil	42.0

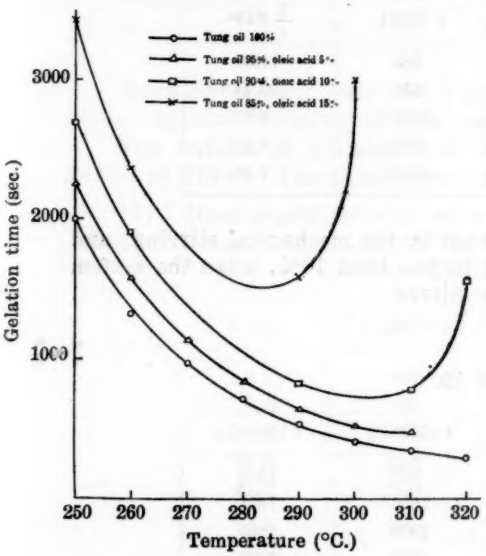

Fig. 2.

calculated from the initial inclination of the lines. The results thus obtained are summarized in the following table.

From the above results it is concluded that the value of x_∞ becomes greater as the degree of unsaturation of fatty acid increases.

The temperature effect of the gelation time of the system added with oleic acid is shown in Figs. 2 and 3.

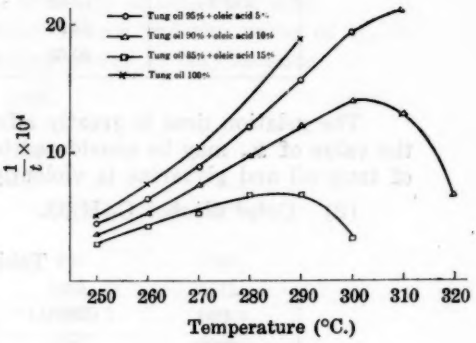
Tung oil 95% + oleic acid 5%
Tung oil 90% + oleic acid 10%
Tung oil 85% + oleic acid 15%
Tung oil 100%
$\frac{1}{t}\times10^4$
20
10
250 260 270 280 290 300 310 320
Temperature (°C.)

Fig. 3.

In general, oleic acid behaves like linseed oil.

II. Fatty Alcohols. Next, the effects of fatty alcohols which from the standpoint of esterification have the natures opposite to those of fatty acids, were measured. Numerical data are shown below.

(1) *Glycerine* (30° Be′).

Table 8.

Temperature	Glycerine added x (%)	Gelation time t (sec.)	$\frac{1}{t}\times10^4$
280°C.	0	674	14.84
	5.25	1589	6.29
	7.76	2731	3.66
	19.20	3650<	2.74>
290°C.	0	436	22.94
	5.11	620	16.13
	9.09	2794	3.58
	11.92	3484<	2.87>

As glycerine does not mix with tung oil, the measurement was carried out by weighing both materials into the test tubes, and the mixture was stirred with a glass rod during the first two minutes while the determination was carried on.

From the $1/t-x$ curve it is seen that the gelation-retarding action of glycerine becomes more intense as the amount of glycerine increases, than it could be expected from the linear relation of initial part. The results obtained without stirring the mixture are shown in Table 9.

Table 9.

Temperature	x (%)	t (sec.)	$\frac{1}{t}\times 10^4$
270°C.	0	885	11.30
	5.26	958	10.44
	10.08	1045	9.57
	13.50	1085	9.22
	20.60	1257	7.96

The gelation time is greatly affected by the mechanical stirring; and the value of x_∞ may be considered to be less than 10%, when the system of tung oil and glycerine is violently stirred.

(2) *Cetyl alcohol* $C_{16}H_{34}O$.

Table 10.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	671	919	1344
5	740	1054	1474
10	897	1309	1965
15	1159	1705	2486

The relation of $1/t$ to x is given by a curved line V, the value of x_∞ becoming 31% when estimated from the data with samples containing 10 to 15% of cetyl alcohol.

(3) *Oleyl alcohol* $C_{18}H_{36}O$.

Table 11.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	665	906	1346
5	763	1097	1542
10	902	1295	1844
15	1210	1619	2256

The general tendency is the same as that of cetyl alcohol and x_∞ becomes 32.5%.

(4) *Mono-glyceride of oleic acid.*

Table 12.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	660	902	1306
5	766	1035	1489
10	998	1388	1887
15	1731	2227	2879
20	3439	4182	4860

Mono-glyceride of oleic acid is prepared as usual by heating glycerine and an equivalent amount of oleic acid with 1% of sulphuric acid.

The relation of $1/t$ and x is nearly linear and the value of x_∞ is 24.5% at 270°C. The gelation-preventing power is very intense.

(5) *Mono-glycol ester of oleic acid.*

Table 13.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	635	902	1300
5.43	724	1030	1512
10.00	863	1231	1728
15.73	1162	1502	2090
20.40	1684	2121	2712

The mono-glycol ester of oleic acid is synthetized in the same way as the case with mono-glyceride. The general tendency is the same as in mono-glyceride, the value of x_∞ amounting to 35%.

Fig. 4 shows the results obtained for four systems of tung oils added respectively with 10, 20% of oleyl alcohol, and 9.7, 13.5% of mono-glyceride.

At elevated temperatures near 300°C. the gelation time reaches a minimum value and again it increases

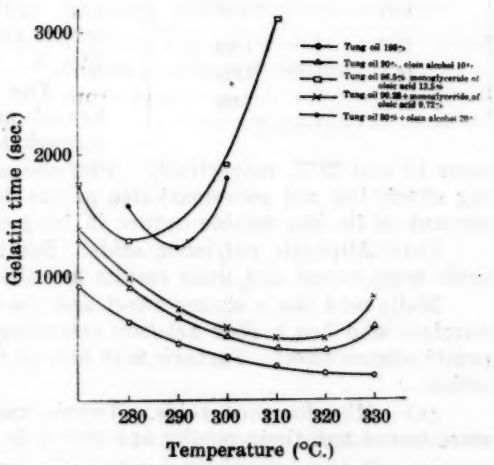

Fig. 4.

as the temperature increases. This tendency is the same as in fatty acids.

The fact that glycerine has a remarkable gelation-retarding action has been reported by Rhodes and Potts, but on the effect of mono-glyceride and fatty alcohols no report has been published.

In the cases of monovalent alcohol such as oleic, cetyl and mono-glycol ester, the values of x_∞ become 33, 31 and 35% respectively. On the other hand in the polyvalent alcohols such as glycerine, glycerine mono-ester, x_∞ amount to 10 and 14%. The peculiar behavior of glycerine is thus anticipated.

It is known that the exchange of glycerine radical occurs when fatty oil is heated with alcohols[4]. Therefore the exchange of alcohol radical plays a part in the gelation-retarding effect of glycerine.

From the results of author's experiments monovalent alcohols have the retarding effect comparable to that of fatty acids. It follows therefore that another consideration should be given for this case.

III. Several Organic Substances. (1) *Hydrocarbons.* (a) Solid paraffin (Solidifying point 53°C.).

Table 14.

Solid paraffin (%)	Gelation time (sec.)
0	1247
15	1719
20	1952

The percentage of solid paraffin added (x) behaves linearly to the reciprocals of the gelation time ($1/t$) and the value of x_∞ is 56%.

(b) Mobile oil A (Boiling range 195~230°C. at 1 mmHg.).

The linear relation also exists in this case between $1/t$ and x, the value of x_∞ being 53%.

Table 15.

x (%)	t (sec.)
10	1102
15	1226
20	1428

(2) *Organic acids.* (a) Aromatic acids. The gelation-retarding effects of benzoic acid, cinnamic acid and phthalic acid anhydride were tested and their results are shown in Fig. 5.

The gelation-retarding effects of benzoic acid and cinnamic acid are very remarkable and the value of x_∞ become 18 and 25%, respectively. Phthalic acid anhydride has also retarding effect, but not so remarkable as the former two acids, probably on account of its less soluble nature in tung oil.

(b) Aliphatic polybasic acids. Succinic, malic, citric and tartaric acids were tested and their results are shown in Fig. 6.

Malic acid has a strong effect and the value of x_∞ is 19% at 270°C. Succinic acid has a poor gelation retarding action and citric acid shows practically no effect. Tartaric acid has, on the other hand, an accelerating action.

(c) Miscellaneous acids. Tannic and gallic acids, and pyrogallol were tested and their results are shown in Fig. 7.

(4) H. H. Young, H. C. Black, *J. Am. Chem. Soc.*, **60** (1938), 2603.

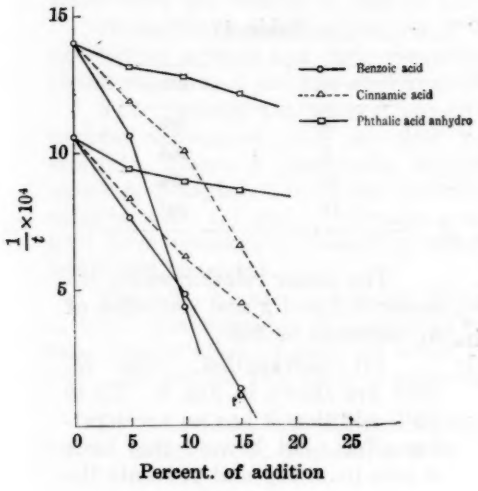

Fig. 5.

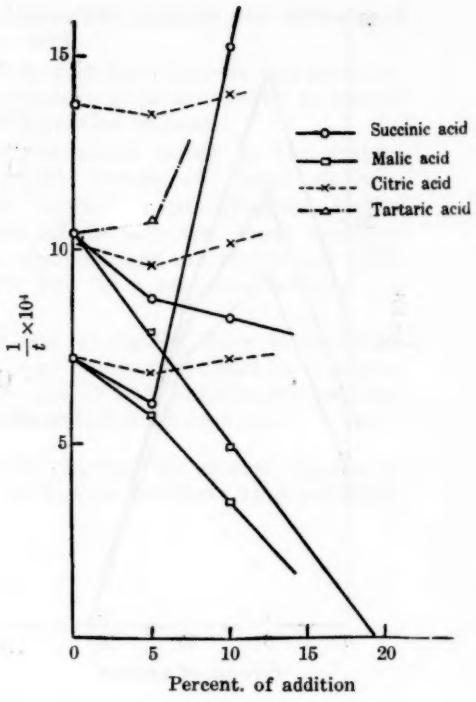

Fig. 6.

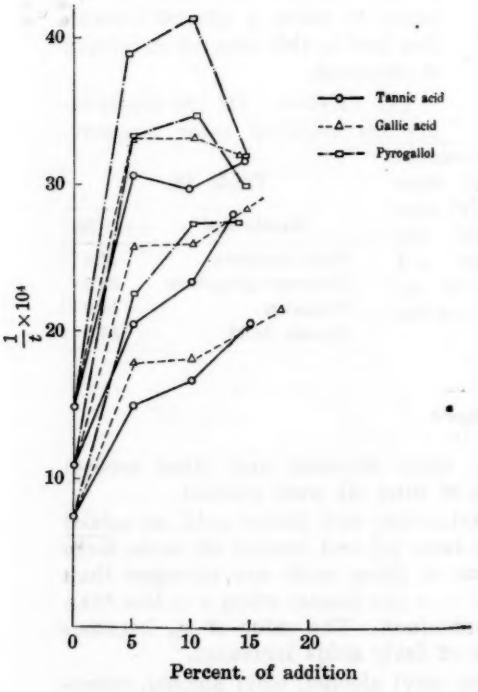

Fig. 7.

These acids have poor solubility in tung oil, but all of them have weak accelerating effects.

(3) *Aromatic substances.*

(a) α-Naphthylamine.

Table 16.

x (%)	t (sec.)
0	898
4.90	1015
9.98	1170
15.0	1381

The linear relation exists between $1/t$ and x and the value of x_∞ becomes 42.3%.

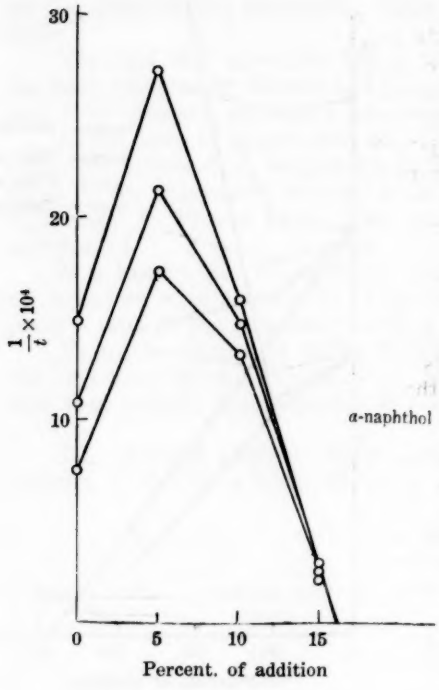

Fig. 8.

(b) Hydroquinone.

Table 17.

x (%)	t (sec.)
0	888
5	908
10	926
15	947

The linear relation exists between $1/t$ and x and the value of x_∞ amounts to 236%.

(c) α-Naphthol. The results are shown in Fig. 8. Up to 10% addition it has an accelerating effect, but beyond this limit it acts inversely and prevents the gelation.

(d) β-Naphthol. The relation between $1/t$ and x appears to form a curved smooth line and in this case no inversion is observed.

(4) *Esters.* Of the plasticizers for cellulose ester lacquers, butyl stearate, tricresyl phosphate, triacetin and Sipalin AOM (methylcyclohexanol ester of adipic acid) were tested. They have also the gelation retarding effects and the linear relations are held between $1/t$ and x in each case. The value of x_∞ at 270°C. are summarized in the following table.

Table 18.

Substances	x_∞ (%)
Butyl stearate	44.8
Tricresyl phosphate	62.5
Triacetin	54.0
Sipalin AOM	57.0

Summary.

(1) The effects of fatty acids, fatty alcohols, and other several organic substances upon the gelation of tung oil were studied.

(2) As simple fatty acids, stearic, oleic and linolic acid, as mixed fatty acids, tung oil, linseed oil, soya bean oil and sesame oil acids were used. The gelation-preventing actions of these acids are stronger than that of fatty oils and the relation of $1/t-x$ are linear, when x is less than 15%, beyond which curved lines are obtained. The value of x_∞ becomes greater as the degree of unsaturation of fatty acids increases.

(3) As fatty alcohols, glycerine, cetyl alcohol, oleyl alcohol, monoglyceride of oleyl acid, monoglycol ester of oleic acid were used. The

gelation-preventing actions of these monovalent alcohols are strong and their order are similar to that of fatty acids.

Glycerine and monoglyceride of oleic acid have very strong gelation-preventing actions and their retarding nature is probably due to special chemical reaction such as exchange of glycerine radicals.

(4) Among the several organic substances tested by the author, neutral substances such as solid paraffin, mobile oil, butyl stearate, triacetin, tricresyl phosphate, Sipalin AOM, α-naphthylamine, hydroquinone, β-naphthol have the retarding effects and the linear relations exist between $1/t$ and x. Benzoic acid, phthalic acid anhydride and malic acid have remarkable retarding effects, but their relations between $1/t$ and x are irregular.

Tartaric, tannic and gallic acids and pyrogallol have accelerating actions. The behavior of α-naphthol is very noteworthy; that is, it accelerates the gelation of tung oil when the amount of addition is less than 10%, but beyond this limit it retards the gelation of tung oil.

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